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## PATENT SPECIFICATION

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### COMPLETE SPECIFICATION

#### A Process of Producing an Alkyl Aryl Sulphonate Detergent

We, CALIFORNIA RESEARCH CORPORATION, a corporation duly organised under the laws of the State of Delaware, United States of America, of 100 West 10th Street, 5 Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a method of producing alkyl aryl sulphonates, primarily useful as detergents, but also useful as surface active agents, wetting agents, and 15 emulsifying agents. More particularly, this invention is concerned with the production of such compounds from the olefinic materials present in hydrocarbon fractions derived from a Fischer-Tropsch process.

20 The production of aryl alkane sulphonate detergents usually involves an alkylation or condensation reaction between olefins and an aromatic hydrocarbon, usually benzene, to produce a aryl alkane compound, followed by 25 a sulphonation of the aryl alkane compound. A paramount problem in the production of a suitable sulphonate detergent has been the provision of a supply of suitable olefins for the alkylation or condensation reaction.

30 Branched chain aliphatic olefins, such as butene polymers, introduce outstanding difficulties because of the instability of these olefins during the alkylation or condensation reactions. In alkylation and condensation 35 reactions with benzene or toluene, there results a degradation of the olefins when excessively branched chain aliphatic olefins are employed. This degradation leads to the production of a mixture of phenyl alkanes 40 containing compounds both lower and higher in aliphatic molecular weight than the olefin originally selected and desired. The instability and degradation of such olefin polymers in the presence of condensation 45 catalysts during alkylating conditions also leads to the production of substantially inseparable poly-alkylated aromatics of the same molecular weight and boiling range as the desired aryl alkane. This is a decided

disadvantage since, upon conversion to the 50 sulphonated aryl derivatives, relatively low yields have resulted. The sulphonated derivatives tend to be relatively poor in detergent quality and require costly purification treatment to eliminate or reduce odor, 55 unsulphonatable residue, color bodies, and other impurities introduced by degradation caused by the original instability of the olefin polymer.

On the other hand, straight chain olefins, 60 particularly 1-olefins, do not have these disadvantages, but heretofore straight chain olefins have been of limited availability and prohibitive in cost. Thus, olefinic hydrocarbons of suitable molecular weight for the 65 production of sulphonated aryl alkane detergents have been available from the cracking by thermal or catalytic processes of petroleum hydrocarbons. While the exact chemical nature of these olefinic materials is not known, 70 they contain naphthenic and aromatic hydrocarbons in addition to olefinic hydrocarbons and exhibit instability and degradation when utilized as a source of olefins in the desired alkylation or condensation reactions. It has 75 now been found that the hydrocarbons obtained from a Fischer-Tropsch hydrocarbon synthesis contain olefins within the molecular weight and boiling point range required for the production of detergents, 80 which olefins are substantially only 1-olefins with few branched chains, so that the olefins derived from this source are highly suitable for the production of desirable aryl alkane compounds by alkylation or condensation 85 reactions. The olefins derived from Fischer-Tropsch hydrocarbons exhibit little degradation or fragmentation and therefore allow the production of desired phenyl alkane materials with a low consumption of the aromatic 90 hydrocarbons. On sulphonation of the aryl alkanes produced using olefins derived from Fischer-Tropsch hydrocarbons there, however, normally is derived a detergent material of inferior quality. The detergent so produced 95 is particularly characterized by inferior wetting powers and odor.

It has now been found that the low quality

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of the aryl alkane sulphonate detergents produced from the use of Fischer-Tropsch olefins is not due to the character of the olefin hydrocarbons themselves from such a source, but rather to the impurities other than olefins normally accompanying such Fischer-Tropsch olefins. The impurities which degrade the quality of the phenyl alkane sulphonate detergents appear to be principally oxygen compounds, particularly aldehydes and ketones. By the use of a separation procedure these oxygen compounds may be readily separated from the Fischer-Tropsch hydrocarbons, and as a result, there is produced a form of olefin-containing stock which is highly desirable for the production of sulphonated aryl alkane detergents. By the use of such stock it is possible to produce detergents light in color, free of odor and of high quality in respect to foaming properties, detergency properties and wetting properties.

The purification of Fischer-Tropsch olefin stocks from the oxygen compounds detrimental to the production of desirable detergents may be carried out according to the invention in various manners, but it has been found that the production of high quality detergents has not so much depended upon the manner of removal of the oxygen compounds as it has upon the completeness of the removal of such compounds however effected. Moreover, it is not believed necessary that all of the oxygen compounds be separated from the olefin stock employed; the principal impurities giving rise to detergents of objectionable odor and color are found to be carbonyl compounds such as aldehydes or ketones, and possibly certain organic acids. These carbonyl and acid compounds may be removed from the Fischer-Tropsch olefin stock in a number of ways, such, for example, as treating the stocks with hot caustic solutions or with sodium bisulphite. By such treatments it is possible to remove from the olefin stock substantially all the oxygen compounds except hydroxy or alcohol compounds. The olefin stocks thus produced may then be utilized for the production of sulphonated phenyl alkane detergents of good quality. Complete removal of oxygen compounds from the olefin stocks remaining after the caustic or sodium bisulphite treatment may be effected in a variety of ways, such, for example, as extraction with solvents. The remaining oxygen compounds are principally higher boiling point alcohols which may be extracted by solvents, such, for example, as methanol. These higher boiling point alcohols might also be removed by azeotropic distillation, such materials as butylene glycol being used for the third phase. A particularly satisfactory method is the use of boric acid solutions. By the use of boric acid solutions

to promote esterification of the higher alcohols, esters are formed which may be readily separated by distillation.

While the foregoing methods of removing oxygen compounds may be employed, it has been found that the purification of the olefins by adsorbents such as activated carbon and silica gel is to be preferred. By the use of a silica gel adsorption, not only is it possible to obtain a separation of olefins and paraffins from Fischer-Tropsch hydrocarbons with complete removal of oxygenated compounds, but it is also possible to separate the olefins from aromatic hydrocarbons. As a result, an olefin-containing hydrocarbon stock is readily derived in one operation which is a superior stock in all respects for the production of sulphonated aryl alkane detergents.

While in the foregoing description we have referred to the use of benzene for the production of phenyl alkanes and sulphonated phenyl alkane detergents, the reaction of olefinic stocks with toluene to form tolyl alkanes and the sulphonation of such tolyl alkanes to form sulphonated tolyl alkane detergents follow the same rules, so that detergents of highest quality may be produced by first removing from the olefins the carbonyl compounds, and using the purified olefinic stocks thus derived for the production of such sulphonated tolyl alkane detergents.

It is an object of this invention, therefore, to provide a process of producing phenyl and tolyl alkanes and sulphonated phenyl and tolyl alkane detergents from Fischer-Tropsch hydrocarbons, which products are free of odorous carbonyl compounds such as aldehydes and ketones.

It is another object of the present invention to provide a process of producing phenyl and tolyl alkanes and sulphonated phenyl and tolyl alkane detergents in which degradation of olefin stock and fragmentation are substantially eliminated and by which detergents may be economically and efficiently produced, which detergents are of high quality.

Other objects and advantages of the process of the present invention will become apparent from the following description of a preferred example of the invention.

Fischer-Tropsch hydrocarbons are derived by hydrocarbon synthesis of hydrogen and carbon monoxide. Such syntheses are performed by passing the hydrogen and carbon monoxide at high temperatures over a catalyst. The particular type of catalytic reaction utilized does not substantially alter the character of the products produced, although it may alter considerably the proportion of the different products, such as oxygenated compounds, olefins and paraffins produced. In the particular example of the process herein described, the Fischer-Tropsch hydrocarbons were obtained by passing

mainly hydrogen and carbon monoxide over an iron alkali catalyst (that is a catalyst consisting essentially of metallic iron and containing a small amount of an alkali metal compound or an alkaline earth compound which acts as an activity promoter) at a temperature of about 600° F. and 300 pounds pressure. By cooling the gases emitting from the reaction first to a temperature of about 350° F. to remove waxes, followed by cooling to about 100° F. to separate an oil fraction from the water produced in the process, the hydrocarbons utilized were separated from the waxes and the oil fraction. The hydrocarbons were then subjected to fractional distillation to separate out an olefin stock having the particular molecular weight or boiling points suitable for the manufacture of detergents. In order to produce efficient sulphonated phenyl and tolyl alkane surface active agents useful as detergents and wetting agents, it is necessary to select the alkane portion in such manner that its hydrophobic character will be sufficiently counterbalanced by the hydrophilic character of the sulphonate grouping to the proper degree. In order to obtain in the product the desired properties, the alkane portion of the molecule should not contain too few or too many carbon atoms. In general, the alkane portion of the molecule should contain not less than 8 carbon atoms nor more than 20 carbon atoms, and it is preferable to restrict this variation to a narrower range, such as between 12 and 15 carbon atoms in order to produce materials of the greatest efficiency. This balance between the hydrophobic and hydrophilic character is conveniently determined in the case of the sulphonated alkanes derived from olefinic materials by the boiling point range of the olefinic material. A hydrocarbon fraction boiling between 300° F. and 600° F. at atmospheric pressure is utilized where it is desired to produce products the alkane portion of which contains between 8 and 20 carbon atoms. It is desirable to use a hydrocarbon fraction boiling between 350° F. and 500° F. at atmospheric pressure. About 95% of the olefinic constituents in such a hydrocarbon fraction will contain between 12 and 15 carbon atoms.

In the particular example given, there was employed a Fischer-Tropsch fraction having an A.S.T.M. distillation of start 360° F.; 5%—371° F.; 10%—374° F.; 50%—400° F.; 90%—449° F.; 95%—465° F.; and end point 571° F. The bromine number of this stock was 63.5, the carbonyl number 28.9, hydroxy number 27.8, and neutralization number 12.4, the carbonyl number and hydroxy number being determined, respectively, by the methods described in J.A.C.S. 57, 57, 1935, and J.A.C.S. 57, 61,

1935, from which analysis it was estimated that the stock contained 63.5% olefins; 12.6% carbonyl compounds; 12.7% hydroxy compounds, and 4.2% acids. There was, therefore, at least 7% of known non-olefinic hydrocarbons or paraffins present.

To separate from this fraction of Fischer-Tropsch hydrocarbons the desired olefin material free from oxygen compounds, the material was subjected to a silica gel adsorbent treatment. This separation was effected by passing the materials through a column containing 28 to 200 mesh silica gel. Silica gel is an active adsorbent possessing the properties of adsorbing many types of chemical compounds. Compounds will be adsorbed to different degrees, depending upon their chemical structure and polarity. It is, therefore, possible even with compounds with relatively small differences in polarity to effect separations of mixtures into their constituents or into groups of constituents having similar polarities and having similar chemical structures. In such an adsorption treatment as applied to Fischer-Tropsch hydrocarbons, the paraffin constituents tend to come through the column first, followed thereafter by the olefinic materials, the aromatic compounds, if any present, following the olefinic material, the oxygen compounds being most strongly retained by silica gel.

In passing this fraction of Fischer-Tropsch hydrocarbons through the silica gel column, it was found that the bromine number of the fractions emerging from the column steadily increased until about 60% of the material had passed through the column, after which the bromine number of the material coming through the column diminished. The first 60% of the material passing through the column was therefore separated from the remainder of the material as the olefin stock for further treatment. This stock exhibited a bromine number of 68, while the carbonyl number, hydroxy number and neutralization number of the stock are zero, from which it was calculated that the stock now consisted solely of olefins and paraffins in proportions of approximately 69% olefins and 31% paraffins. By the process, therefore, substantially complete removal of carbonyl compounds, hydroxy compounds and acidic compounds from the olefinic material was attained in one operation. Examination of the olefin material present in the stock retained for use indicated that it was substantially exclusively 1-olefins having little branched chain structure.

This olefin stock containing the olefines and paraffins was then utilized for the preparation of mono-phenyl alkanes. For this purpose, any well-known method of alkylating aromatics might be employed. Alkylation is carried out, for example, by use of the

Friedel-Crafts type condensation catalyst, such, for example, as  $\text{AlCl}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$ ,  $\text{BF}_3$ , or mixture of  $\text{BF}_3$  and  $\text{HF}$ , a particularly effective catalyst being hydrogen fluoride. In this case hydrogen fluoride was employed as the catalyst and the alkylation was carried out by the process described in U.S. Patent No. 2,275,312, which describes a process for alkylating aromatic hydrocarbons by employing hydrogen fluoride as a catalyst.

About four parts by weight of benzene were mixed with 1 part by weight of the silica gel treated olefinic material to be processed. The ratio, however, of benzene to olefinic material is not critical and may vary over considerable limits. A temperature of  $100^\circ\text{F}$ . was selected as a suitable temperature of treatment. Treated product was then separated and washed and the unreacted benzene distilled off. The alkylated product was then fractionally distilled at atmospheric pressure. The first portion of the distillate amounting to approximately 15% by weight of the alkylated product was separately removed and set aside as undesirable material for sulphonation. The distillation was continued and the next portion of the distillate, amounting to approximately 70% by weight of the alkylated product, was segregated for sulphonation. This fraction boiled in the range  $525^\circ\text{F}$ . to  $650^\circ\text{F}$ . at atmospheric temperature. The remaining 15% of the alkylated product constituted the still bottoms and was discarded as an unsuitable material for sulphonation. The heart cut fraction, amounting to 70% of the alkylated product and boiling in the range  $525^\circ\text{F}$ . to  $650^\circ\text{F}$ ., was sulphonated and neutralized to produce a phenyl alkane detergent in the manner described hereinafter. This fraction was subjected to sulphonation in the usual manner. While sulphonation may be carried out by any usual process of sulphonating alkyl aromatics, using sulphuric acid of strength such as from 98% to 20% fuming or higher, sulphonation was carried out by the use of 20% fuming acid using about 3 moles of sulphuric acid per mole of hydrocarbon material. Temperatures of about  $110^\circ\text{F}$ . to  $140^\circ\text{F}$ . may be employed, but the temperature range of  $130^\circ\text{F}$ . to  $140^\circ\text{F}$ . was utilized. The unsulphonated oil was then separated from the sulphonated oil, the unsulphonated residue being about 3.3% of the starting material, by weight.

The product was then neutralized with sodium hydroxide to produce a mixture of sodium sulphonates and sodium sulphate. The ratio of sodium sulphonates to sodium sulphate was then adjusted to 40:60. The product produced was odorless, a 1% aqueous solution thereof giving a 20 color by the Saybolt method. The product was subjected to tests for efficiency as a detergent, for wetting properties and foaming properties.

These tests established that the sulphonated phenyl alkanes thus produced from the Fischer-Tropsch olefins were fully equal, if not superior, to previously known detergents of this class in such properties.

While in the example just described the benzene was reacted with the purified olefins to provide first a phenyl alkane which was thereafter sulphonated to produce the desired detergent, either benzene or toluene may be utilized to form such a desired alkyl aryl sulphonate detergent. By the substitution in the example given of toluene for benzene in a substantially similar manner, a tolyl alkane is first produced which is then sulphonated in a substantially similar manner to produce the sulphonated tolyl alkane detergent.

While the particular example of the invention herein described is well adapted to carry out the objects of the present invention, it is obvious that various modifications and changes may be made, and this invention includes such modifications and changes as come within the scope of the appended claims.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of producing alkyl aryl sulphonate detergents from an olefine-containing hydrocarbon fraction boiling under normal pressures between  $300^\circ\text{F}$ . and  $600^\circ\text{F}$ . and consisting essentially of the reaction products which have been obtained in the Fischer-Tropsch synthesis of hydrocarbons, which comprises improving the wetting power and odor of said detergent by substantially completely removing carbonyl compounds from said hydrocarbon fraction, thereafter alkylating benzene or toluene with the olefine-containing hydrocarbon fraction to form aryl alkanes, and sulphonating said aryl alkanes.

2. A process of producing alkyl aryl sulphonate detergents from olefine-containing hydrocarbon fraction boiling under normal pressures between  $300^\circ\text{F}$ . and  $600^\circ\text{F}$ . and consisting essentially of the reaction products which have been obtained in the Fischer-Tropsch synthesis of hydrocarbons, which comprises improving the wetting power and odor of said detergent by substantially completely removing oxygenated organic compounds from said hydrocarbon fraction, thereafter alkylating benzene or toluene with the olefine-containing hydrocarbon fraction to form aryl alkanes, and sulphonating said aryl alkanes.

3. A process as claimed in claim 2, wherein the oxygenated organic compounds are removed by subjecting the said hydrocarbon fraction to a silica gel adsorption treatment to separate a fraction containing olefin constituents free of oxygenated organic compounds.

4. A process as claimed in claim 1 or 3, wherein the hydrocarbon fraction boils under normal pressure between 350° F. and 500° F.
5. A process as claimed in claim 3 or 4, wherein the fraction separated by silica gel adsorption treatment is a high bromine number fraction, derived while the bromine number of the material passing from the adsorbent is increasing.
- 10 6. In a process of producing alkyl aryl sulphonate detergents from an olefine-containing hydrocarbon mixture boiling within the range of from 300° F. to 600° F. under normal pressure and consisting
- 15 essentially of the reaction products which have been obtained in the hydrogen-carbon monoxide Fischer-Tropsch hydrocarbon synthesis, said mixture containing oxygenated compounds forming derivatives under alkyl-
- 20 ating and sulphonating conditions which are deleterious to wetting power and odor in said sulphonate detergent, said process comprising alkylating benzene or toluene
- with said olefin-containing hydrocarbon mixture to form an aryl-substituted alkane and 25 sulphonating said alkane to an alkyl aryl sulphonate detergent, the step of removing said oxygenated compounds prior to said alkylation by selective adsorption of said oxygenated compounds from said olefinic 30 hydrocarbon mixture.
7. An alkyl aryl sulphonate detergent whenever prepared or produced by the methods or processes claimed in any of the preceding claims, or their obvious chemical 35 equivalents.

Dated this 6th day of October, 1948.

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